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Measuring the Tilt Angle of ODTMS Self-Assembled Monolayers on Al Oxide Surfaces.

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Abstract

Adsorbed octadecyltrimethoxysilane (ODTMS) on native aluminium oxide substrates have been studied with near-edge X-ray absorption fine structure (NEXAFS) spectroscopy in order to determine the average tilt angle of the surface film. Previous experiments have shown that the time-dependant adsorption isotherm of ODTMS on Al exhibits oscillatory adsorption. In this work we present the findings of our tilt angle studies for Al samples dipped in a 0.75% ODTMS solution at various times during oscillatory adsorption. It clearly can be seen that the alignment of the surface film is related to the coverage, hence for a minimum in the film coverage (at 65 sec dip time) the tilt angle of the ODTMS film is found to be ~50° relative to the surface normal. Below the minimum in the film coverage (at 30 sec dip time) the tilt angle has been found to be ~41° whereas for samples dipped above the minimum film coverage (at 80 and 95 sec) the angles are ~46° and ~45° respectively. These measurements indicate a strong correlation between film alignment and film coverage during oscillatory adsorption.

Keywords: X-ray absorption spectroscopy, polycrystalline surfaces, organic/inorganic interfaces, coatings, self-assembly using surface chemistry, order-disorder phase transitions.

1. Introduction

Organosilane polymers can be readily tailored to include a terminal functional group that allows the molecule to act as a coupling agent between dissimilar surfaces [1]. As such, there is a great deal of interest in organosilanes as coupling agents for a variety of technological applications [2]-[4]. The unique properties of organosilanes have also attracted interest in the field of electronically active polymer surfaces. For example, γ-aminopropyltriethoxysilane (γ-APS) has been used to produce aligned layers of liquid crystal material on silicon oxide surfaces [5], [6]. Haloalkylsilanes have been used to produce biomolecular assemblies of genetically engineered surface proteins [7]. Photoactive thin films of coumerin (a laser dye) have been fabricated using trimethoxysilane [8]. Moreover, organosilanes have also been shown to be electronically active and have themselves been used as the active layer in electroluminescent devices [9]. In addition, it is well-known that a characteristic feature of many alkylsiloxanes is their tendency to form self assembled monolayers (SAMs) on hydrophilic substrates [10]-[12]. With recent developments in the electronic device fabrication area, where research of SAMs acting as electron carriers in devices has been carried out [13], the understanding of the adsorption mechanisms and film growth of these materials on metallic substrates are becoming increasingly important. Consequently, research in the area of organosilane adsorption continues to develop rapidly but given the complexity involved in organosilane adsorption process it is understandable that many of the molecular mechanisms involved still remain unclear [3], [4].

Previous research, aimed at understanding these processes, have revealed the complex nature of organosilane-metal interactions [14], with the identification of a so-called *oscillatory adsorption* phenomenon [15], on a range of metal oxide surfaces [16]-[19], where molecules attach strongly during initial film growth but subsequently desorb (if left for a period of time), then reattach at a later time.

In this paper we discuss our findings on measuring the tilt angle of octadecyltrimethoxysilane (ODTMS) on aluminium at assorted dip times. ODTMS is an excellent 'model molecule' to study with NEXAFS in order to gain understanding of the initial processes of organosilane adsorption and especially film alignment. ODTMS consists of a relatively long alkyl chain, which makes it ideal for carbon K-edge NEXAFS measurements, and also tends to form self assembled monolayers. Understanding the adsorption and orientation mechanisms in this model system is a first step in tailoring organosilane molecules for electronic polymer applications.

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2. Experimental

Polycrystalline Al samples of 99.99% purity were abraded, cleaned and dipped in 0.75% (v/v) ODTMS solution of pH 4 for various dip times. Subsequently, the samples were dried and stored individually under a nitrogen atmosphere [18],[20].

NEXAFS experiments were performed at the Pohang Accelerator Laboratory in Korea. Spectra were recorded at various incident angles between 20° and 90°, measured between the direction vector of the incident linear polarised light and the surface plane of the sample. Hence, for an angle of 90° the electric field vector, **E**, will be parallel to the surface plane whereas at 20°, **E** is almost perpendicular to the surface plane. Spectra were acquired at the carbon K-edge using total electron yield (TEY) and have been normalised as discussed by Watts et al [21] and the changes in the C K-edge structure have been used to ascertain the preferential orientation of molecules within the surface coating.

3. Results and Discussion

The orientation of an adsorbed organic molecular film on substrates can be determined by the technique of angle-resolved NEXAFS [21]. By measuring the carbon K-edge, which contains information about the C-H bonds and C-C bonds at energies of ~287 eV and ~293 eV respectively, the overall tilt angle of the molecules in the organic film can be obtained.

Figure 1 shows a total yield carbon K-edge spectrum for ODTMS on aluminium dipped for 20 sec. A step edge has been fitted along with a number of characteristic peaks. The important peaks for the analysis involved in this work are those at ~287 eV and ~293 eV, which are associated with the Rydberg states (R*) and the C-C σ* resonances respectively [23]-[25]. The contributions due to these states are shown in figure 1.

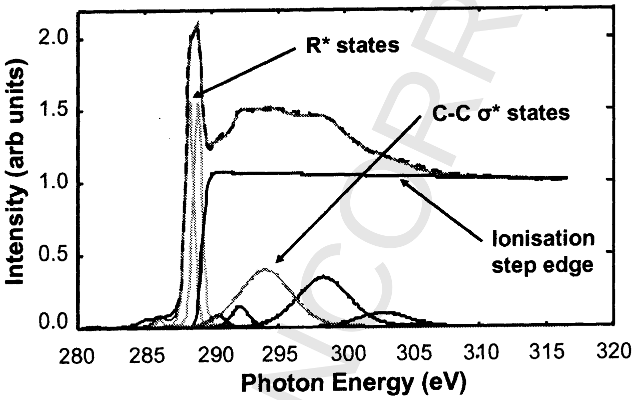

Fig. 1: The C K-edge NEXAFS spectrum for ODTMS on Al for 20 sec dip time. The underlying grey line is the original spectrum, while the dashed black line is the best fit. The Gaussian-Lorentzian peaks correspond to the various characteristic peaks fitted to the data after subtracting a step edge. The values for the position and widths of these fitted peaks are in agreement with the accepted literature values [21].

A given bond in a molecule will readily absorb photons if it is aligned in the same direction as the polarisation vector of the synchrotron radiation. Hence, by analysing the contributions due to the Rydberg states and C-C σ* resonances a film polarisation dependence will be evidenced for aligned alkyl chains since these orbital states are mutually orthogonal. By measuring the C K-edge NEXAFS spectrum over a range of tilt angles, and then peak fitting, the relative contributions of these two orbitals as a function of angle can be extracted.

A quantitative analysis of the surface tilt angle therefore requires modeling the overlap of the vector orbital with the polarization of the incident beam and then comparing this model with the experimental data. The functional form of this model is well established [21]. Briefly, the angular dependence of the measured NEXAFS intensity for vector orbitals that are parallel and perpendicular to the polarization vector of the incident X-ray beam are given by the following set of equations [21]:

$$I_v^{\parallel} = ⅓[1 + ½(3\cos^2\theta - 1)(\cos^2\alpha_1 + \cos^2\alpha_2 + \cos\alpha_1 \cos\alpha_2 - 1)] \tag{1}$$

$$I_v^{\perp} = 1/6[3 - \cos^2\alpha_1 - \cos^2\alpha_2 - \cos\alpha_1 \cos\alpha_2] \tag{2}$$

$$I_p^{\parallel} = 2/3[1 - 1/4(3\cos^2\theta - 1)(\cos^2\gamma_1 + \cos^2\gamma_2 + \cos\gamma_1 \cos\gamma_2 - 1)] \tag{3}$$

$$I_p^{\perp} = 1/6[3 + \cos^2\gamma_1 + \cos^2\gamma_2 + \cos\gamma_1 \cos\gamma_2] \tag{4}$$

where $I_v^{\parallel}$ is the resonance intensity for a vector orbital interacting with the electric field component of the photon beam that lies parallel to the synchrotron storage ring. Similarly, $^{\perp}$ denotes an interaction with the electric field component that lies perpendicular to the storage ring (vertical). The *p* subscript denotes the interaction of a set of orbitals arranged in essentially a planar formation where the normal vector of the said plane corresponds to the axis of the modelled molecule. θ is the angle of X-ray incidence relative to the surface and α and γ are polar tilt angles of the molecular adsorbate.

Combining the above equations, it is possible to obtain the following set of equations [21]

$$I_v = A[P\, I_v^{\parallel} + (1 - P)I_v^{\perp}] \tag{5}$$

$$I_P = B[P\, I_p^{\parallel} + (1 - P)I_p^{\perp}] \tag{6}$$

where A and B are constants and P is the degree of linear polarisation in the plane of the synchrotron storage ring and hence the orbit of the electron beam.

Equations 5 and 6 provide us with a tool for finding the tilt angle of our surface molecules by simply measuring the angular intensity dependence of the Rydberg states (R*)